

SOME PROBLEMS IN THE USE OF HYDROCARBONS
IN FUEL CELL POWER SYSTEMS

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INTRODUCTION

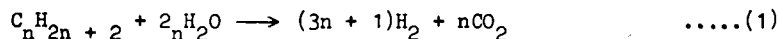
Because of the difficulty of making hydrocarbons react directly in low temperature fuel cell systems, there is considerable interest in hydrocarbon-reforming systems that produce hydrogen for fuel cell power plants. However, most of the technology for the steam-reforming of hydrocarbons has been concerned with large plants for which the throughput of hydrogen has been measured in millions of cubic feet per hour rather than in the hundreds of cubic feet per hour which are of more concern to the fuel cell power system designer concerned with the production of a few kilowatts of electrical power. This means that complexities in plant that can be tolerated in a hydrogen-production plant intended for the chemical industry are often quite unacceptable in a simple power unit that must be operated by unskilled personnel. In constructing a fuel cell power system one has the opportunity to modify the design of both the hydrocarbon-reforming system and also the fuel cell itself in order to achieve a satisfactory compromise between cost, simplicity and reliability. The particular compromise arrived at in any given circumstance will depend considerably on the conditions under which the power system is called upon to operate. In this paper some of the variables at the disposal of the designer will be considered and suggestions made regarding the most fruitful approaches to certain of the problems.

As far as the hydrocarbon-reforming unit is concerned, the most important factors facing the designer are the degree of purity of fuel that is acceptable to the reforming unit and the degree of purity of hydrogen that is acceptable to the fuel cell. Whereas most low temperature fuel cells made to date have used alkaline electrolytes, those with acid electrolytes have received attention recently, and this trend obviously has a strong influence on the purity of the gas required by the fuel cell. Initially, low temperature fuel cells with alkaline electrolytes were the easier to develop and they required pure hydrogen. The advent of the palladium/silver diffuser capable of giving ultra-pure hydrogen from a source supplying impure hydrogen encouraged the development of hydrogen generators suited to the limitations of the alkaline fuel cell. However, it is now possible to contemplate the operation of fuel cells with acid electrolytes and a number of examples have been given in recent years of electrodes that will tolerate various impurities in the feed gas. Use of this type of electrode is considered in this paper and the generation of hydrogen is considered from both aspects, viz. that of producing an ultra-pure product and that of producing a less pure one for use with the electrodes developed more recently.

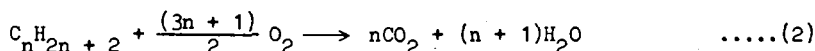
The first section of this paper will be concerned with some of the problems encountered in the design of the hydrocarbon-reforming system and the second section will deal with electrodes for use on impure hydrogen.

HYDROCARBON REFORMING SYSTEMS

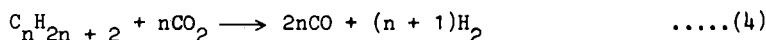
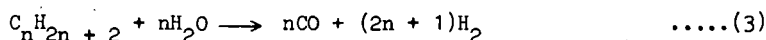
In obtaining hydrogen from hydrocarbons one has the choice of using a steam hydrocarbon-reforming reaction,



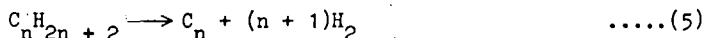
an oxidative reaction,



which is highly exothermic and is followed by

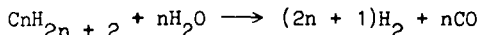


or a cracking reaction,

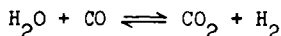


Generally speaking, a fuel cell power system will be developed because of its attractively high efficiency compared with that of the alternatives. Therefore it would seem desirable to make hydrogen generation as highly efficient as possible. Thus, while there may be special occasions when the simple cracking reaction is attractive, generally this will not be so because the resultant hydrogen contains only a small proportion of the total energy of the fuel entering the system. Although oxidative reactions, such as the Shell gasification processes for heavy oil, can be used successfully on a large scale, their success requires the availability of pure oxygen and for this reason such processes are not normally attractive for use in small power sources. It is possible to operate this type of reaction on air with added steam, to give a gas which contains about 40% hydrogen. This is rather dilute for application in fuel cell systems. However, a major disadvantage of the oxidative process is that, since it involves combustion, particles of elementary carbon are produced which are almost impossible to eliminate from the system without extensive treatment. Such particles vary in size from several microns down to a few Angstroms in diameter, and are extremely difficult to filter from the gas stream. Fine carbon particles would be expected to give trouble over long periods as they would accumulate at points where the gas flow is subjected to a sharp change in direction such as one can expect to find in the passages that occur in fuel batteries. On the other hand, the steam-reforming reaction can give hydrogen concentrations of the order of 70% on a dry basis, the gas being free from particulate contamination. If a hydrocarbon which is low in sulphur content is available and acceptable to the user, then this process is extremely attractive. In normal commercial practice, when customers wish to purchase a fuel for the generation of hydrogen by the steam-reforming process, fuel of extremely low sulphur content is usually specified since its use simplifies the overall process. Correspondingly, it seems reasonable to adopt this practice for small fuel cells where the small scale of the system reinforces the need for simplicity.

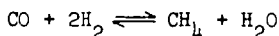
It is useful, in the first instance, to consider the equilibria involved in the generation of hydrogen-rich gases from the hydrocarbon, via the straight-forward steam reforming reaction,



followed by the water gas reaction



and the methanation reaction



With the availability of computer programs the overall effect of these equilibria in given circumstances can readily be calculated. In Table 1 are given typical equilibria for a mixture of a hydrocarbon and water. The ratio chosen of three molecules of water to each molecule of carbon in the feed stock can with modern catalysts give reliable operation on a variety of hydrocarbons up to and including kerosines with a significant aromatic content. Covered by Table 1 are the effects of pressure and of the removal of water from the feed after it has been through the catalyst stage. Results are given for two operating temperatures, 527°C and 827°C.

Inspection of these columns immediately indicates the embarrassment of choices facing designers. The lower operating temperature is attractive because it limits the possibility of carbon deposition on the catalyst and the consequent reduction of catalyst life. Additionally the efficiency of the system is likely to be greater since less heat exchange will be necessary. Finally, if operation under pressure is contemplated, then the selection of alloys suitable for use under pressure at 500°C is much easier than for use at 750°C. A lower operating temperature implies the possibility of a more rapid start-up of the power system, and this is sometimes of importance. If one wishes to purify the hydrogen by means of a palladium/silver diffuser, operation under pressure is necessary in order to limit the area of diffuser required. Whereas at 500°C and 20 atmospheres a considerable proportion of methane is generated, at 750°C the gas has a high carbon monoxide content. However, this carbon monoxide content can be reduced by the injection of further water and use of a low temperature shift catalyst; under suitable conditions this will reduce the carbon monoxide content to a few tenths of a percent and increase the hydrogen concentration accordingly. Without the additional injection of water for this purpose, the hydrogen content of the gas from the reformer before water has been "knocked-out" is only about 42%. This means that either one must use a large area of diffuser to obtain a satisfactory yield of hydrogen, and this brings with it problems of weight, volume and expense, or, alternatively, some arrangement must be made to remove water from the system. This latter involves reducing the temperature to the point at which condensation occurs (at 20 atmospheres this is about 180°C) and then reheating the gas to 350°C, a temperature suitable for operation of the palladium/silver diffuser. In the two systems so far developed of which the authors are aware, namely that developed by Engelhardt Industries for the U.S. Army Signal Corps and that developed by the Pratt and Whitney Company for the U.S. Army Electronics Command, water knock-out does not appear to have been used and the disadvantages of a large area of diffuser appear to have been accepted. Because of the cost and complexity of high pressure operation it is clear that operation at low pressure is preferable in the interests of simplicity and the low cost of the reformer unit.

If an impure gas is fed to the fuel cell there are certain attractions in passing all the gas through to the fuel cell and then burning the effluent from the fuel cell to supply process heat. In this case it is, of course, essential to ensure that the effluent from the fuel cell is a combustible gas. When the course of using an impure gas is adopted, then the advantages of operating at the lower

feed temperature of 500°C for the steam-reforming catalyst become evident. Whereas for operation at 750°C it is often necessary to specify a fuel which is not far removed from a mixture of straight hydrocarbons, fuels containing up to at least 15%w of aromatic compound are acceptable with suitable reforming catalysts operating at 500°C or below.

Since nickel-containing catalysts are normally used for steam-reforming of hydrocarbons and these catalysts are sensitive to sulphur, the sulphur-content of the fuel has a dominant role in performance. In Figure 1 is shown the time to "kerosine breakthrough" for a typical steam-reforming catalyst when fuels of similar composition but varying sulphur content were used. These were in fact made by blending a fuel of low sulphur content with one of high sulphur content, so that the sulphur compounds are representative of those likely to be encountered in practical fuels. Whereas with a fuel sulphur content of 20 parts per million the life of a catalyst was in excess of 1200 hours, at 1500 parts per million sulphur life had fallen to a mere eight hours. While it is possible to use additional catalyst as a "sulphur guard" this is a very expensive way of desulphurizing fuel and normally one would prefer to specify a fuel of low sulphur content to simplify the operation of the fuel cell. This seems a small price to pay for the high efficiency of the fuel cell.

ELECTRODES FOR USE WITH IMPURE HYDROGEN

Whereas operation on pure hydrogen is a relatively straightforward matter and electrodes are available that operate satisfactorily for thousands of hours, the situation is more complicated when one wishes to operate on gas taken directly from the reformer. Even if the carbon monoxide is reduced to a very low concentration by a suitable catalyst for the methanation reaction (3) as was done by Meek & Baker¹ problems can still arise from the presence of carbon dioxide. In Figure 2 are shown results indicating that at 25°C slow poisoning of a platinum electrode occurs with the mixture of 80%v hydrogen/20%v carbon dioxide. This presumably occurs by the "reduced carbon dioxide" mechanism of Giner². However, this can be overcome by the use of alloy catalysts, as is also shown in Figure 2 by the example of the platinum/ruthenium catalyst. If on the other hand the feed contains appreciable amounts of carbon dioxide together with carbon monoxide, then extremely rapid poisoning of platinum occurs and it becomes essential to use an alloy catalyst. It is also advantageous to operate at as high an electrolyte temperature as possible. The effect of gas composition in terms of hydrogen and carbon monoxide contents is shown in Figure 3 and it will be noted that there are marked advantages in operating with as low a carbon monoxide content as possible. If it is borne in mind that it is the effluent from the last fuel cell of a battery that will determine the operating conditions of the battery itself there would seem to be a strong argument in favour of reducing the carbon monoxide content as much as possible by use of a suitable shift catalyst. In Table 2 are examples that illustrate the advantage which can be obtained from a shift catalyst without any further addition of steam to the feed. If one were aiming at a reformer efficiency of about 60% then the effluent from the fuel cell would contain about 40% of the total input heat necessary for use as process heat. This would imply that if the inlet hydrocarbon contained about 0.6% carbon monoxide the outlet from the cell would contain 1.4% carbon monoxide and the electrode characteristics would be better than those shown for 2% carbon monoxide in the diagram. It should be emphasized that these characteristics are not the optimum that can be achieved but are representative of the advantages of using alloy catalysts in these circumstances to obtain a higher performance. The catalyst loading could be increased by a factor of three, from the twelve milligrams per square centimeter used to 36 milligrams per square centimeter, but whether the increase in performance obtained would be worthwhile would depend upon individual circumstances. It may be noted in passing that whereas hydrogen containing carbon monoxide fed to an electrode with a simple platinum catalyst causes a steady drift

in potential towards that of the oxygen electrode, a completely steady output is obtained with alloy catalysts. This difference would appear to exist as direct oxidation of carbon monoxide takes place on the alloy catalyst electrode leaving vacant sites for the further oxidation of hydrogen. An alternative is to use a pure platinum catalyst and operate at 150°C where oxidation of carbon monoxide on the platinum occurs at a satisfactory rate. However, operation at this higher temperature involves the use of a phosphoric acid electrolyte giving higher internal resistance, slower starting of the cell and additional corrosion problems.

SUMMARY AND CONCLUSIONS

Since low temperature fuel cell power systems that utilize hydrocarbon fuels are likely to be expensive, most applications for which they are chosen will demand long unattended periods of operation because it is only under these conditions that fuel cells are likely to show to economic advantage. In order to achieve the necessary reliability for this type of operation, it is essential to keep the number of moving parts in the system to a minimum and to use electrodes with as long a life as possible. All the evidence suggests that the lower the operating temperature of electrodes, the longer the life. For example, "Shell" Research electrodes have operated unchanged at 30°C for periods of 15,000 hours on hydrogen and oxygen, and this figure relates to a 17-cell battery and so is not a freak performance of an individual electrode. On the other hand, if one goes to temperatures of 150°C or more, then electrode life can be something of a problem. As has been shown, operation at pressure involves complications in addition to the expense of the diffuser required for the production of ultra-pure hydrogen and therefore the impure hydrogen system has much to commend its use. The data presented in the preceeding section of this paper suggest that it is well worthwhile to use an alloy catalyst on the electrode, and to "shift" the carbon monoxide content to as low a level as convenient. To some extent this will be determined by the power level required and the cost of the electrode system.

Bearing in mind the necessity to operate efficiently under part-load conditions when losses in the battery will be at a minimum it will probably be desirable for the battery to be fairly compact in order to minimize heat loss and maintain a reasonably high equilibrium temperature. Consequently the narrow passages of the cell are likely to require a pump or blower to move air through the battery. From the point of view of silence and reliability there is much to commend the use of a centrifugal blower and, for the small quantities of air likely to be involved with most power systems, the arguments in favour of the electrodes which will operate at a minimum pressure are strong.

With the electrodes and reforming catalysts now available there seems to be no problem in assembling reliable fuel cell power generators to use impure hydrogen. As will have become clear from the previous section of the paper the authors are strongly in favour of using fuels of minimum sulphur content. As in all work with low temperature fuel cells, the outstanding problem is of course the cost and availability of platinum catalysts and it will be most interesting to see how successfully they can be eliminated or at least reduced in quantity in practical power systems.

A substantial amount of the work discussed in this paper has been carried out under Ministry of Defence contracts and acknowledgement is accordingly made for permission to publish the information so obtained.

REFERENCES

1. J. Meek and B.S. Baker. "Fuel Cell Systems" - Advances in Chemistry, Series 47, American Chemical Society 1965, p.221.
2. J. Giner. Electrochemica Acta, 8, 857, 1963.

Table 1

Steam-hydrocarbon reaction equilibria

Feed composition, %v

	$C_nH_{2n} + 2 + 3nH_2O$				$C_nH_{2n} + 2 + 3nH_2O$ after water "knockout"			
	1 atmosphere		20 atmospheres		1 atmosphere		20 atmospheres	
	527°C	827°C	527°C	827°C	527°C	827°C	527°C	827°C
H ₂	34.7	47.9	12.1	42.4	59.8	70.5	31.1	66.8
CO	2.5	12.0	0.4	9.9	4.3	17.7	1.0	15.6
CO ₂	12.6	8.0	9.4	8.4	21.7	11.8	24.2	13.2
CH ₄	8.2	0.01	17.0	2.8	14.2	0.015	43.7	4.4
H ₂ O	42	32.1	61.1	36.5	-	-	-	-

Table 2

Effect of shift catalyst on gas composition
from reformed kerosineFeed $C_nH_{2n} + 2 + 3nH_2O$

	Composition, %v, wet basis	
	From reformer at 527°C	After shift at 227°C
H ₂	34.7	37.02
CH ₄	8.2	8.2
CO ₂	12.6	14.92
CO	2.5	0.18
H ₂ O	42.0	39.68

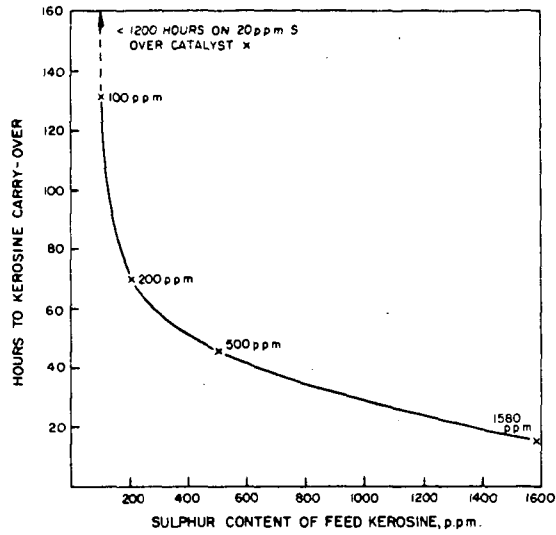


FIG. 1—Effect of sulphur content of kerosine on time taken for kerosine carry-over to be observed when steam-reforming over catalyst x

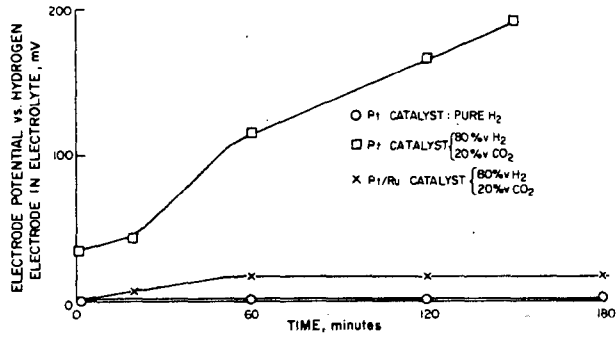


FIG. 2—Effect of carbon dioxide on electrode performance: 175 mA/sq. cm, 25°C

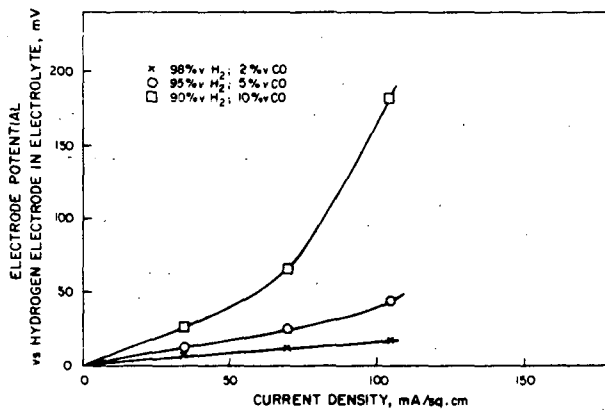


FIG. 3—Effect of carbon monoxide on alloy hydrogen electrode performance: electrolyte 6N H₂SO₄, 70°C